Chemistry 2740 Spring 2011 Test 3

Time: 50 minutes
Marks: 32
Aids allowed: calculator, 8.5×11-inch formula sheet
Useful data is given on the reverse of this page.
Instructions: You can answer the questions in any order, but make sure that you clearly label each of your answers with the question number in your exam booklet(s).
If you use a graph to answer a question, make sure to provide a reasonable sketch of the graph, as well as a brief explanation of what information the graph provides.

1. State whether each of the following statements is true or false, and explain **briefly** how you reached your conclusion. [2 marks each]

   (a) It is possible to measure the activity coefficient of a single ion in solution.

   (b) If, for a certain reaction, $E^\circ > 0$, then that reaction is thermodynamically allowed.

   (c) The reaction $Fe(CO)_5 + OH^- \rightarrow (CO)_4FeH^- + CO_2$ is probably not elementary.

2. As you know, we often see the pH defined as $-\log_{10}[H^+]$ rather than the more correct definition based on the activity of the hydrogen ion. How large a difference does this make? Using Debye-Hückel theory, calculate the difference between the correct and approximate (concentration-based) definitions of pH for a 0.01 mol/L HCl solution at 25 °C. [8 marks]

3. Silicon atoms enter the upper atmosphere either from interplanetary dust or from the evaporation of meteoroids as they enter the atmosphere. These silicon atoms can then react either with oxygen or with ozone to form silicon oxides. The following is one of the elementary reactions that can occur:

$$Si_{(g)} + O_{2(g)} \xrightarrow{k} SiO_{(g)} + O_{(g)}$$

   (a) Give the mass-action rate law for this elementary reaction. [2 marks]

   (b) This reaction has been studied under conditions in which oxygen was present in great excess. The following pseudo-first-order rate constants were measured at different oxygen concentrations at 190 K:[1]

$[O_2]/10^{-6}\,\text{molL}^{-1}$	0.052	0.284	0.879	1.12	1.63	2.152
$k'/10^5\,\text{s}^{-1}$	0.090	0.322	0.798	1.01	1.59	1.91

      i. Explain why a graph of k' vs $[O_2]$ will give the second-order rate constant k. What should the intercept of this graph be? [4 marks]

      ii. Determine k, and discuss whether the value of the intercept you calculated is in reasonable agreement with your theoretical prediction. [8 marks]

      iii. For the experiment with an oxygen concentration of 1.12×10^{-6} mol/L at 190 K, how long would it take for 90% of the silicon atoms to react? [4 marks]

[1] J. C. Gómez Martín, M. A. Blitz and J. M. C. Plane, *Phys. Chem. Chem. Phys.* **11**, 671 (2009).

Useful data

$\varepsilon_0 = 8.854\,187\,817 \times 10^{-12}\,\mathrm{C^2 J^{-1} m^{-1}}$
$R = 8.314\,472\,\mathrm{J\,K^{-1} mol^{-1}}$
To convert degrees Celsius to Kelvin, add 273.15.
For water at 25 °C, $\varepsilon_r = 78.54$.
$\ln \gamma_\pm = -A\,|z_+ z_-|\,(\varepsilon T)^{-3/2}\,\sqrt{I_c}$ where $A = 1.107 \times 10^{-10}$.